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(54) Title: **RECEIVER MEDIUM FOR DIGITAL IMAGING**

(57) Abstract: A receiver medium for digital imaging comprises a substrate having a dye-receiving surface bearing a coating comprising a highly branched functionalised polymer of generally globular form, e.g. a dendrimer, dispersed in a host polymer. Functional groups at or near the surface of the branched polymer, may interact with and bind dye molecules having complementary functional groups, eg dyes as disclosed in WO 96/34766, e.g. by acid-base interaction, thus having the effect of chemically fixing the dye within the coating on the receiver medium. Because dye molecules can be chemically bound to the branched polymer in the receiver sheet, it is possible to use host polymer materials of lower T_g than generally required in the prior art, with the host polymer typically having a T_g of less than 50 °C. This means that dye molecules can have a significantly increased diffusivity through the coating, prior to interaction, resulting in a more even distribution of dye through the coating than has been possible hitherto. The invention also covers a method of making the receiver medium, a method of printing, and a receiver medium/dye combination.

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 785 088 A (AGFA GEVAERT NV) 23 July 1997 (1997-07-23) page 2, line 48 - line 52 page 4, line 44 - line 52	1-16
Y	page 5, line 8 - line 20	17-20
Y	WO 96 34766 A (ICI PLC ;BRADBURY ROY (GB); MOSCROP CLIVE (GB); SLARK ANDREW (GB);) 7 November 1996 (1996-11-07) cited in the application page 4, line 7 -page 13, line 15 page 16, line 18 - line 25	17-20

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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EP 0785088	A	23-07-1997	JP 9193560	A	29-07-1997
WO 9634766	A	07-11-1996	DE 69603952	D	30-09-1999
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Title: Receiver medium for digital imaging

Field of the Invention

This invention relates to a receiver medium for use in digital imaging, and concerns a receiver medium for such use, a method of making such a medium, a method of printing using such a medium and a receiver medium/dye combination.

Background to the Invention

Traditionally, photographs have been created by capturing a latent image on silver halide sensitised film, and then transforming the latent image into a colour reproduction of the original subject by a series of chemical processes. Overall the process is characterised by a continuous (analogue) relationship between an original image and the resulting print. Prints produced in this way have acceptable stability to various invasive agents such as fingergrease and also to fading by light.

In recent years the advent of digital cameras has allowed the capture of images in an electronic digital form, and their subsequent manipulation and printing without recourse to the use of silver films and associated chemical processing. This offers the possibility of substantial control over the whole process, which can now be performed in the home or office by a wide portion of the general population. It is predicted by some that digital imaging will in time substantially replace traditional photographic methods.

Printing processes used for digital imaging include thermal dye transfer printing and ink jet printing.

Thermal dye transfer printing is a generic term for processes in which one or more thermally transferable dyes are caused to transfer from a dyesheet to a receiver in response to thermal stimuli. Using a dyesheet comprising a thin substrate supporting a dyecoat containing one or

more such dyes uniformly spread over an entire printing area of the dyesheet, printing can be effected by heating selected discrete areas of the dyesheet while the dyecoat is pressed against a receiver sheet, thereby causing dye to transfer to corresponding areas of that receiver. The shape of the pattern transferred is determined by the number and location of the discrete areas which are subjected to heating. Full colour prints can be produced by printing with different coloured dyecoats sequentially in like manner, and the different coloured dyecoats are usually provided as discrete uniform print-size areas in a repeated sequence along the same ribbon-like dyesheet.

High resolution photograph-like prints can be produced by thermal dye transfer printing using appropriate printing equipment, such as a programmable thermal print head or laser printer, controlled by electronic signals derived from video, computer, electronic still camera, or similar signal generating apparatus. A typical high speed thermal print head has a row of individually operable tiny heaters spaced to print six or more pixels per millimetre, using very short hot pulses.

Receiver medium for thermal dye transfer printing generally comprises a substrate sheet supporting a receiver coat of a dye-receptive composition containing a material having an affinity for the dye molecules, and into which they can readily diffuse when an area of dyesheet pressed against it is heated during printing. Such receiver coats are typically around 2 to 6 μ m thick, and materials with good dye-affinity are generally thermoplastic polymers, such as saturated polyesters, soluble in common solvents to enable them readily to be coated onto the substrate from solution.

In ink jet printing, a stream of charged ink droplets is projected onto ink receptive receiver medium at high velocity, eg up to 20 m/s. Movement of the ink jet may be computer controlled, and images may be formed and printed rapidly. By using inks of different colours a full colour image can be produced. In general, ink jet printing inks are water-based compositions that are usually dye-based solutions. Such inks are widely used in a range of ink jet printers, for commercial, office and domestic use including desk-top printers. A receiver medium for use in ink jet printing generally comprises a substrate carrying an ink absorbent layer that typically comprises a polymer or a mixture of polymers, eg cellulosic

polymers such as carboxymethyl cellulose and especially hydroxyethyl cellulose; gelatins; vinyl polymers such as a polyvinyl alcohol and polyvinyl pyrrolidone; and acrylic polymers such as polyacrylic acid.

For convenience, dyes and inks for use in digital imaging techniques will be referred to generally as dyes.

Both the above printing methods suffer from the fact that the resulting images generally comprise dyes kinetically frozen in polymeric layers which are at a temperature below their T_g , ie the dye molecules are physically entrapped in the polymer in the form of a solid solution and are not chemically bound in position. Any changes resulting in the system being above the polymer T_g , eg due to thermal energy or ingress of swellants, plasticisers or contaminants such as fingergrease, are liable to result in dye migration which in turn can lead to dye crystallisation and loss of colour density or image blurring and loss of resolution.

It is also known in the art of digital imaging, and in particular thermal dye transfer printing and ink-jet imaging technologies, that dyes printed into low T_g polymeric receiver materials suffer image degradation as a result of dye migration over time. To overcome this, most current imaging systems employ receiver media with relatively high T_g polymers which are stable at room temperature, typically having a T_g of at least 60°C. High T_g receiver systems, however, typically suffer from low dye diffusion rates during the printing process, which in turn results in high dye concentrations near the surface of the image and subsequently poor image stability with respect to light and physical contact.

One approach to improving image stability in thermal dye transfer printing is to apply a polymeric protective layer, either as a separate panel from a thermal transfer dyesheet, or in a separate lamination step. However, this approach can result in image blurring caused by thermal stimulation on application of the layer and also has the drawback of requiring extra material in the form of a separate panel or lamination sheet.

Another approach to improving image stability in thermal dye transfer printing is to arrange for the image dyes to be interactive with the receiver layer. For example, it has been proposed to render dyes immobile by the following methods:

- 1) Acid-base interactions. Here the dyes contain eg two or more acid groups that can form strong interactions with basic groups attached to the receiver polymer, eg as described in WO 96/34766.
- 2) Chelation. US 5,512,531 of Konica discloses the interaction of dyes with metal ions in the receiver by a chelation process.
- 3) Cationic dyes. EP 506,034 of Sony describes the use of cationic dyes with receivers containing layered inorganic materials. These layered materials are capable of absorbing the charged cationic dyes, and holding them in a stable environment.

Finally, performance may be improved by reacting an appropriate dyestuff with the receiver layer, resulting in the formation of a covalent bond to attach the dye to the receiver.

It is a feature of all these interactive methods that insufficient heat is available to allow the dyes to migrate sufficiently to permit the development of the full interaction, and hence to realise the full potential stability of the system. Indeed stratification of the dye at the surface (ie concentration of dye at the surface of the receiver medium) is a particular problem with these systems. The significance of this problem has led to proposals to use acid vapour treatment to fix an image (US 4,880,769), and to use low Tg receiver polymers containing organic acid groups or low Tg receivers containing oligomeric and polymeric acids to reprotonate deprotonated cationic dyes (US 5,627,956).

Summary of the Invention

In one aspect the present invention provides a receiver medium for digital imaging, comprising a substrate having a dye-receiving surface bearing a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer.

The extent of branching of a polymer can be defined in terms of the degree of branching, ie the proportion of monomer units carrying a branch. A polymer that is fully branched, that is in which each monomer unit carries a branch, thus has a degree of branching of 1, while a linear, non-branched polymer has a degree of branching of 0. The term "highly branched polymer" is used herein to mean a polymer having a degree of branching of at least 0.5. Such polymers are sometimes also referred to as hyperbranched polymers. The growth pattern of branching may be regular or irregular. Polymers with a degree of branching of 1 (perfect branching) and a regular growth pattern are known as dendrimers. Figure 1 is a representation of a dendrimer, having a degree of branching of 1 and a regular growth pattern, and Figure 2 is a representation of a polymer with a degree of branching of 1 and an irregular growth pattern, both having a tree-like form. It is thus possible, but not essential, for the highly branched polymer to be a dendrimer.

The degree of branching itself is not determinative of the three dimensional shape or form of the polymer. The branched polymers useful in the invention, as well as being highly branched, must be of generally globular form. The term "generally globular form" means non-linear and non-planar in form, having significant extent in all directions and preferably having generally similar dimensions in all directions, ie being generally spherical in form. The ratio of the maximum dimension:minimum dimension of the branched polymer is preferably $\leq 4:1$, more preferably $\leq 3:1$. Dendrimers and similar structures with irregular or regular growth patterns (eg as shown in Figures 1 and 2) are of generally globular form, as branching and growth occurs outwardly in three dimensions, as are polymers of similar form but with a lesser degree of branching, and so are all suitable for use in the present invention. Also suitable are so-called star polymers, which comprise a central core from which a number of branched polymer strands (of the same or different molecular structure) radiate outwardly.

Highly branched polymers of generally globular form, eg dendrimers, have a large number of terminal or end groups per unit molecular weight, typically concentrated at or near the surface of the molecule. The highly branched polymer is functionalised, that is, at least some of the end groups carry functional groups eg selected from: OH, NH₂, NHR, NR₂,

COOH, CONH₂, NHCOR, CONHR, SO₂NH₂, SO₂NHR, SO₃H, NHCONH₂, NHCONHR, =NOH and PO₃H, in which R is selected from CH, NO₂, Cl, F, Br, C₁₋₆alkyl, C₁₋₆alkoxy, NHCOC₁₋₆alkyl, NHCOnphenyl, NHSO₂alkyl, NHSO₂phenyl and aryloxy, more preferably from the groups having at least one H atom. Such functional groups at or near the surface of the branched polymer may interact with and bind dye molecules having complementary functional groups, eg dyes as disclosed in WO 96/34766, eg by acid-base reaction, thus having the effect of chemically fixing the dye within the coating on the receiver medium. Such functional groups on the polymer may optionally additionally or alternatively form cross-links with the host polymer. Further, by appropriate molecular design and synthesis and selection of appropriate functional groups it is possible to construct branched polymeric materials with either a hydrophilic surface, eg by use of primary amine functional groups, or a hydrophobic surface, eg by use of functional groups such as alkyl chains. The ability to vary the hydrophobicity of the polymer surface provides the capability of producing polymers with optimum solubility characteristics within the host polymer. The functional groups are thus selected with regard to factors including the nature of the host polymer, and the type of dyes with which the receiver medium is intended for use.

In general, the greater the extent of functionalisation of the highly branched polymer the better. Preferably at least 50%, more preferably at least 70%, of the end groups carry functional groups as discussed above, with the functional groups preferably being at or near the surface of the highly branched polymer so as to be accessible to dye molecules.

The chemistry of the remainder of the highly branched polymer is generally unimportant.

The highly branched polymer typically has a molecular weight of at least 1000.

The radius of gyration of the highly branched polymer in a suitable good solvent is preferably in the range 2 to 10 nm.

Highly branched polymers of generally globular form, eg dendrimers, have low viscosity relative to their molecular weight compared with linear polymers. The reduced viscosity has benefits for processing and handling of the polymers in terms of ease of use, incorporation in

liquid coatings etc, and also means it is possible to use polymers of higher molecular weight than would otherwise be the case. The reduced viscosity also allows solutions with very high solids content to be used as coatings.

Suitable highly branched polymers, eg dendrimers, may be synthesised using known techniques and are available commercially eg from Aldrich.

The advantage of such highly branched polymers over crosslinked polymer particles is that they present very large surface areas for interaction with dye molecules, are readily soluble in coating solvents and do not present significant light scattering or other optical defects by virtue of their being molecular in nature.

The host polymer is selected having regard to the digital imaging technique for which the receiver medium is intended for use, ie thermal dye transfer printing or ink jet printing. Suitable polymers are well known to those skilled in the art. For thermal dye transfer printing, polymers such as polyesters, poly(vinyl pyridine), vinyl pyrrolidone/vinyl acetate, vinyl chloride/vinyl acetate copolymers, cellulosic materials, polycarbonate etc may be used, while for ink jet printing, polymers such as vinyl polymers, acrylic polymers and cellulosic polymers such as carboxymethyl cellulose and hydroxyethyl cellulose may be used. The host polymer may be crosslinked in a known manner. The host polymer is preferably relatively inert and unreactive with respect to the dye molecules with which the medium is intended for use, with the host polymer having no or only a few groups capable of interacting strongly with the dye. Thus the host polymer should have low affinity for the dye compared with the affinity of the dye for the highly branched polymer, with the dye being freely soluble in the host polymer, so that the dye is able to move freely through the host polymer and thus reach and interact with the highly branched polymer. Suitable mixtures of host polymers may be used. Host polymers are generally linear (non-branched).

Because the invention enables dye molecules to be chemically bound to the branched polymer in the receiver sheet, it is possible to use host polymer materials of lower T_g than are generally required in the prior art. This means that dye molecules can have a significantly increased diffusivity through the coating, prior to interaction, resulting in a

more even distribution of dye through the coating than has been possible hitherto, particularly avoiding high dye concentrations at or near the coating surface.

The host polymer thus preferably has a $T_g < 50^\circ\text{C}$, and more preferably $< 25^\circ\text{C}$. Good results have been obtained using the polyester Vylon 103 (Vylon is a Trade Mark) from Toyobo, which has a T_g of 47°C as the host polymer in a receiver medium for use in thermal dye transfer printing. Vylon 103 has good compatibility with a wide range of dyes.

Certain commercially available highly branched polymer products as supplied include an amount of generally linear, non-highly branched polymer, and it is possible that this non-highly branched content of the highly-branched product may function as the host polymer.

The highly branched polymer is suitably present in an amount in the range 10 to 90%, preferably 20 to 60% by weight of the coating.

The highly branched polymer is dispersed throughout the host polymer and functions as a molecular heterophase, presenting a very large surface area within the host polymer. By dispersed is meant a system which either shows no large scale heterogeneity (ie $> 1\mu\text{m}$), or else if heterogeneity does exist the refractive indices of the two polymers are suitably matched. The highly branched polymer is substantially immobile within the host polymer at room temperature due to its large molecular size. Immobility can be enhanced, if required, by low level cross-linking of surface functional groups of the highly branched polymer with the host polymer, eg using epoxides or melamine chemistry, to form an interpenetrating network with the host polymer.

The substrate is typically in the form of a film or sheet of suitable material. Typical substrate material include polymeric materials having suitable properties including dimensional stability, optical transparency, translucency or opacity, tensile strength, adhesion characteristics, thermal stability, hardness etc for the intended purpose. Transparent polymeric substrate materials suitable for use in the production of transparencies include sheets or films of polyester eg poly(ethyleneterephthalate) (PET) such as Melinex (Melinex is a Trade Mark) or poly(ethylenenaphthalate) (PEN). Polycarbonate sheets may

also be used for this purpose. Such transparent sheets typically have a thickness in the range about 50 μ m to about 150 μ m. Other possible polymeric materials include polysulphones, polyvinyl chloride, polystyrene, polyimides, polyolefins, polymethyl methacrylate, cellulose esters such as cellulose acetate etc. A wide range of paper, card and laminated materials may also be used as the substrate.

To promote adhesion of the ink absorbent layer to a polymeric substrate, it is often desirable first to treat a surface of the substrate with a priming medium. Creation of a priming layer is conveniently effected by treating a surface of a polymeric substrate with an agent known in the art to have a solvent or swelling action on the substrate polymer. Examples of such conventional agents, which are particularly suitable for the treatment of a polyester substrate, include a halogenated phenol dissolved in a common organic solvent e.g. a solution of p-chloro-m-cresol, 2,4-dichlorophenol, 2,4,5- or 2,4,6-trichlorophenol or 4-chlororesorcinol in acetone or methanol. In addition, and preferably, the priming medium may contain a partially hydrolysed vinyl chloride-vinyl acetate copolymer. Such a copolymer conveniently contains from 60 to 98% of vinyl chloride, and from 0.5 to 3% of hydroxyl units, by weight of the copolymer. The molecular weight (number average) of the copolymer is conveniently in a range of from 10,000 to 30,000, and preferably from 16,500 to 25,000. Desirably the priming layer comprises a polyester material.

If desired, a plurality of priming layers may be sequentially applied to the substrate of receiver medium according to the present invention.

The priming medium is suitably applied at a concentration level which will yield a priming layer having a relatively thin dry coat thickness, for example generally less than 2 μ m, and preferably less than 1 μ m.

The coating is conveniently formed by mixing the coating materials with a suitable solvent or solvent mixture, as is known in the art. The coating materials may be applied by any suitable coating technique, including those known in the field, eg by use of a Meier bar, by roller coating, rod coating, slide coating, curtain coating, doctor coating etc. The coating may then be dried in a known manner.

The coating may be applied to the entire surface of the substrate or to only selected areas of the substrate surface. In the case of a sheet or film of substrate, the coating will typically be applied to at least one surface and possibly both surfaces (to enable double-sided printing).

Drying of the coating may be effected by conventional drying techniques, for example by suspending the coated substrate in a hot air oven maintained at an appropriate temperature. A drying temperature of about 130°C is usually suitable for a polyester substrate.

The thickness of the coating when dry may vary over a wide range, but is conveniently in the range 1µm to 100µm, preferably 50µm or less, especially in the range from 2µm to 10µm, for media for use in thermal dye transfer printing and in the range 10µm to 50µm for media for use in ink jet printing.

The coating desirably includes particulate filler material, to modify the mechanical properties of the coating and also (for media for use in ink jet printing) to modify the porosity of the coating. Suitable materials for this purpose include inorganic, organic or polymeric particulates such as silica including amorphous silica, crystalline silica, fumed silica, alumina, aluminium trihydrate, calcium carbonate, glass, clays, aluminium silicates, polyolefin particulates, organic pigments and mixtures thereof. Particulate filler material has a tendency to increase light scattering, reducing coating transparency, so this factor must be taken into consideration in relation to transparent substrates and coatings, while being of less relevance to opaque receiver media. The particulate filler material may additionally act to increase surface roughness of the coating, thus reducing the tendency of the coating to block, ie stick by wetting action to adjacent surfaces. Filler material particles suitably have a primary size in the range 5nm to 50µm. Fillers with a dimension much smaller than the wavelength of light can be used at higher loadings than larger fillers (because of their lower scattering) and therefore make a greater contribution to the mechanical properties of the coating, but are less efficient at creating surface roughness than are fillers with a major dimension of comparable size to the coating thickness. It is often desirable to incorporate fillers of two different sizes in order to optimise the overall properties of the coating.

The receiver medium may include an optional top coat (or supercoat) over the coating, as is known in the art.

The receiver medium may optionally include one or more back coats on the side of the substrate remote from the dye-receiving surface. These are generally based on a cross-linked polymer binder, and are provided to fulfil a number of different roles, including providing increased friction to improve printer feed, providing antistatic properties and preventing transfer of dyes from one receiver sheet to another.

Other additives may optionally be included in the coating to improve properties of the coating. For example, anti-static materials may be included. As a further possibility lubricants and release agents, such as waxes and silicones, may be included in media for use in thermal dye transfer printing to reduce friction and/or adhesion at the coating surface.

In a further aspect, the invention provides a method of making a receiver medium, comprising applying to a dye-receiving surface of a substrate a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer.

The receiver medium is typically used for digital imaging, eg by ink jet printing or thermal dye transfer printing, in known manner.

In another aspect, the invention thus provides a method of printing, comprising applying dye to the dye-receiving surface of receiver medium in accordance with the invention by a digital imaging technique.

A further aspect of the invention provides a digital imaging receiver medium/dye combination in which the receiver medium comprises a substrate having a dye-receiving surface bearing a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer, and the dye is capable of interacting with the highly branched polymer.

In use of a receiver medium in accordance with the invention, in preferred embodiments at least, dye molecules are able to move freely through the host polymer, resulting in good penetration and distribution of dye throughout the coating. The dye molecules interact with the highly branched polymer that is dispersed throughout the coating, and become fixed in position with good distribution throughout the coating, ie without undesirable concentration at the surface. By suitable adjustment of the coating it may be possible to arrange for some degree of stratification of the dye, with slightly higher concentrations of dye being bound slightly away from the coating surface where the dye is less vulnerable to fading, abrasion etc, without being concentrated too far from the coating surfaces which would result in poor image quality.

The invention will be further described, by way of illustration, in the following Examples, and with reference to the accompanying drawings, in which:

Figure 1 is a schematic representation of a dendritic polymer, having perfect branching and a regular growth pattern;

Figure 2 is a schematic representation of a hyperbranched polymer, having perfect branching and an irregular growth pattern;

Figure 3 is a graph of relative density versus distance (in μm) showing density profiles, before (full line) and after (dashed line) exposure to tetrahydrofuran (THF) vapour, across a printed edge of an acid functional dye printed onto a receiver medium comprising Vylon 103;

Figure 4 is a graph similar to Figure 3 showing results using a receiver medium comprising Vylon 103 and containing 25% by weight dendrimer; and

Figure 5 is a graph similar to Figure 3 showing results for similar receiver media, with and without dendrimer, before and after heating to 75°C for 45 days, with results for medium without dendrimer before heating shown by hatched line and after heating shown by dashed

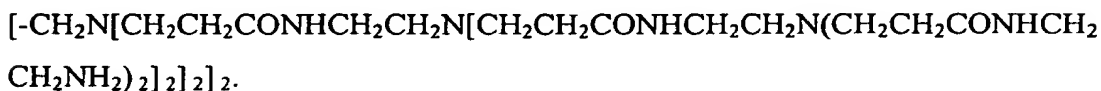
line, and results for medium with dendrimer before heating shown by full line and after heating shown by dot dash line.

Example

The following formulation was prepared and coated onto a synthetic laminate paper substrate using a K5 Meier coating bar to give a wet coated film approximately 36µm thick. The substrate comprises a cellulose core, voided polypropylene layers and a whitening layer on the front surface. The film was then dried by air and cured at 110°C for 90 seconds.

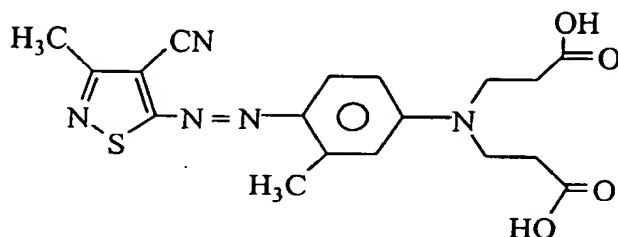
Starburst dendrimer, generation 2 (20% solids in methanol), supplied by Aldrich	1.25g
Vylon 103 polyester, supplied by Toyobo	0.75g
Toluene (solvent)	3.36g
Methyl ethyl ketone (solvent)	5.02g
Beetle 692 (melamine crosslinker (for Vylon and Tegomer), 50% solids), supplied by BIP	0.004g
PK3 (di-N-butylamine blocked para toluene sulfonic acid) 28% solids in methanol	0.004g
Tegomer 2311 (Hydroxy functional siloxane (to impart release properties)), supplied by T.H. Goldschmidt	0.002g

The Starburst dendrimer has a molecular weight (Mn) of 3256 and has the following formula:



The Starburst dendrimer has 16 primary amino surface functional groups.

The dried film was then printed with a dyesheet bearing an acid functional dye (known as S167434) using a thermal dye transfer printer. The dye S167434 has the following structure:-



The acid functional dyesheet was prepared by coating with a K3 Meier bar a 4.2 wt% solution in THF (1:2 dye to poly(vinyl butyral) (supplied by Sekisui) binder ratio) onto 6µm polyester film supplied by Diafoil (Diafoil is a Trade Mark) precoated with a heat resistant back coat. The coated dyesheet was dried at 110°C for 30 seconds. For reference, a comparative receiver film comprising Vylon 103 at the same percentage solids of resin was prepared and printed in the same way.

The edge profiles of the printed films were then examined, perpendicular to the print head alignment, using a Sakura PDM5 scanning microdensitometer, manufactured by Konishiroku, in reflection mode. Two experiments were then performed on separate samples, the first where the samples were exposed to THF vapour for 120 minutes and the second where the samples were heated at 75°C for 45 days. After each period the edge profiles were re-recorded and the results are shown in Figures 3 to 5. The dye is very soluble in THF, and THF has the effect of swelling the coating.

Figure 3 show results using a receiver medium comprising Vylon 103 without dendrimer and demonstrates that after 120 minutes exposure to THF vapour diffusion has clearly taken place. In contrast, Figure 4 shows that with receiver medium in accordance with the invention, including dendrimer, no diffusion has taken place after 120 minutes exposure to THF.

Figure 5 shows results for Vylon 103 receiver medium, with and without dendrimer, before and after heating at 75°C for 45 days. Diffusion is clearly less in samples including dendrimer.

Claims

1. A receiver medium for digital imaging, comprising a substrate having a dye-receiving surface bearing a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer.
2. A receiver medium according to claim 1, wherein at least some of the end groups of the highly branched polymer carrying functional groups selected from OH, NH₂, NHR, NR₂, COOH, CONH₂, NHCOR, CONHR, SO₂NH₂, SO₂NHR, SO₃H, NHCONH₂, NHCONHR, =NOH and PO₃H, in which R is selected from CH, NO₂, Cl, F, Br, C₁₋₆alkyl, C₁₋₆alkoxy, NHCOC₁₋₆alkyl, NHCOnphenyl, NHSO₂alkyl, NHSO₂phenyl and aryloxy, and preferably from the groups having at least one H atom.
3. A receiver medium according to claim 1 or 2, wherein at least 50%, preferably at least 70%, of the end groups of the highly branched polymer carry functional groups.
4. A receiver medium according to any one of the preceding claims, wherein the highly branched polymer has a molecular weight of at least 1000.
5. A receiver medium according to any one of the preceding claims, wherein the radius of gyration of the highly branched polymer is in the range 2 to 10nm.
6. A receiver medium according to any one of the preceding claims, wherein the host polymer is selected from polymers including polyesters, acrylic polymers, vinyl polymers, poly(vinyl pyridine), vinyl pyrrolidone/vinyl acetate, vinyl chloride/vinyl acetate copolymers, and cellulosic polymers.
7. A receiver medium according to any one of the preceding claims, wherein the host polymer has a T_g <50°C.

8. A receiver medium according to any one of the preceding claims, when the highly branched polymer is present in an amount in the range 10 to 90%, preferably 20 to 60%, by weight of the coating.
9. A receiver medium according to any one of the preceding claims, wherein the substrate is in the form of a film or sheet of material.
10. A receiver medium according to any one of the preceding claims, wherein the substrate is pre-treated prior to application of the coating.
11. A receiver medium according to any one of the preceding claims, wherein the coating has a thickness in the range 1 μ m to 100 μ m, preferably 50 μ m or less, especially in the range from 2 μ m to 10 μ m, for media for use in thermal dye transfer printing and in the range 10 μ m to 50 μ m for media for use in ink jet printing
12. A receiver medium according to any one of the preceding claims, wherein the coating includes particulate filler material.
13. A receiver medium according to any one of the preceding claims, including a top coat over the coating.
14. A receiver medium according to any one of the preceding claims, including one or more back coats on the side of the substrate remote from the dye-receiving surface.
15. A method of making a receiver medium, comprising applying to a dye-receiving surface of a substrate a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer.
16. A method of printing, comprising applying dye to the dye-receiving surface of receiver medium in accordance with any one of claims 1 to 14 by a digital imaging technique.

17. A digital imaging receiver medium/dye combination in which the receiver medium comprises a substrate having a dye-receiving surface bearing a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer, and the dye is capable of interacting with the highly branched polymer.
18. A combination according to claim 17, wherein the receiver medium is in accordance with any one of claims 2 to 14.
19. A combination according to claim 16 or 17, wherein the dye has functional groups complementary to functional groups of the highly branched polymer.
20. A combination according to claim 17, 18 or 19, wherein the highly branched polymer and dye are capable of interacting by acid-base reaction.

1/4

Fig.1.

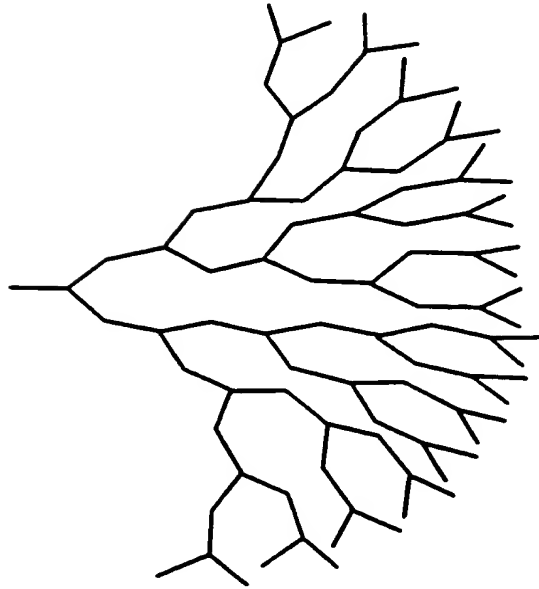
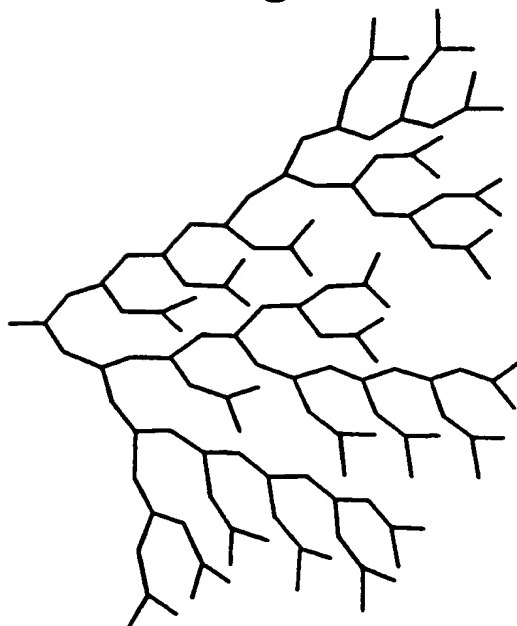
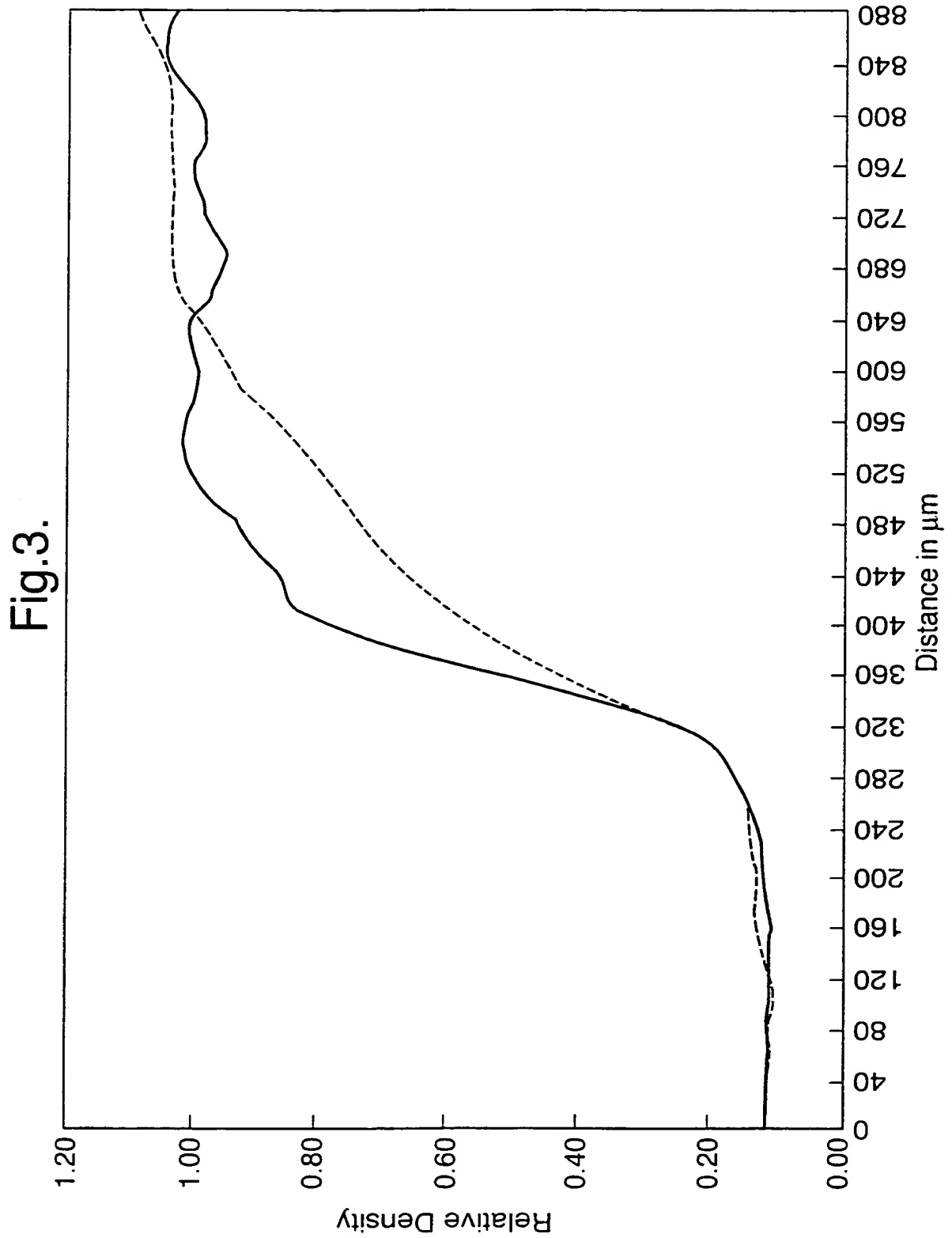
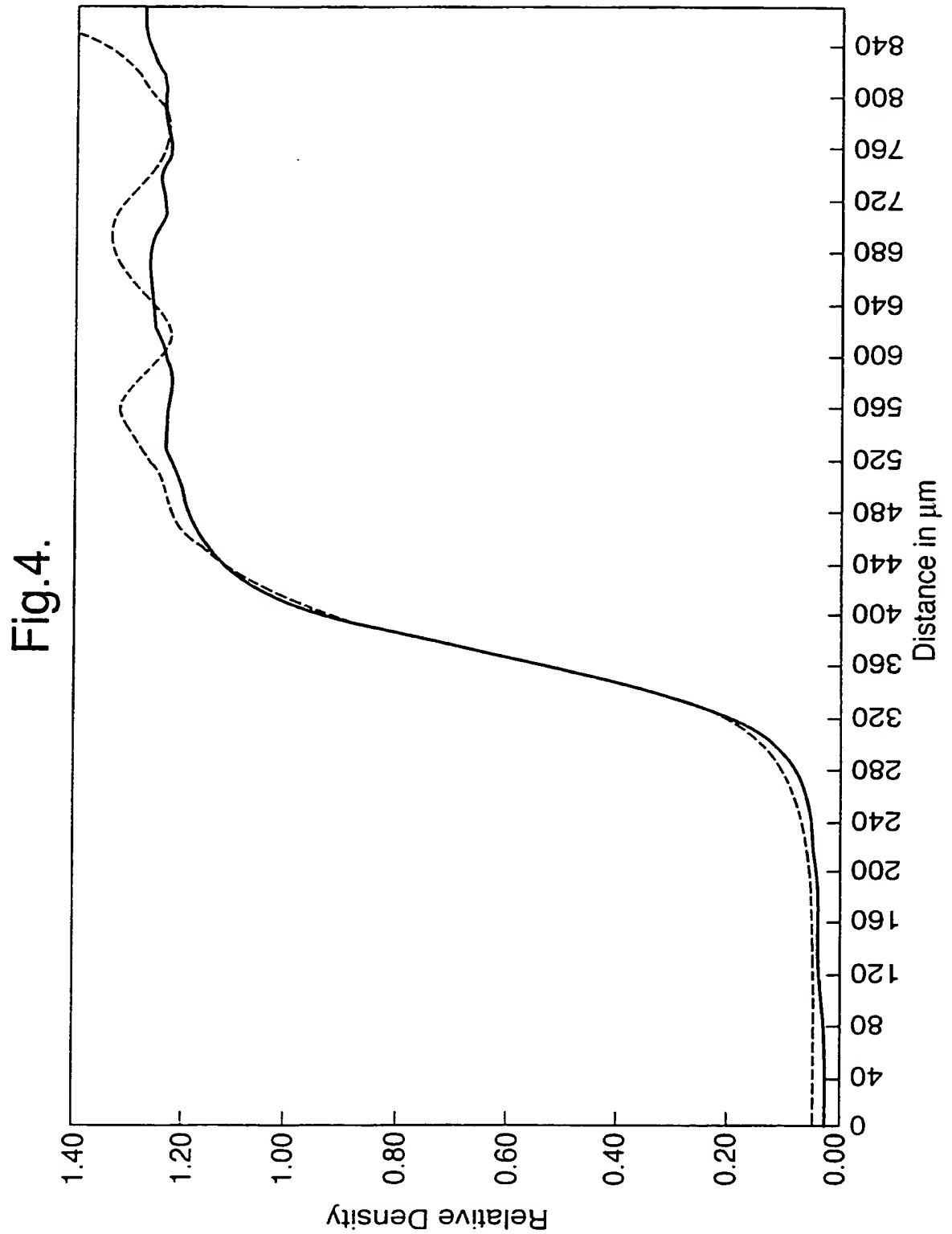
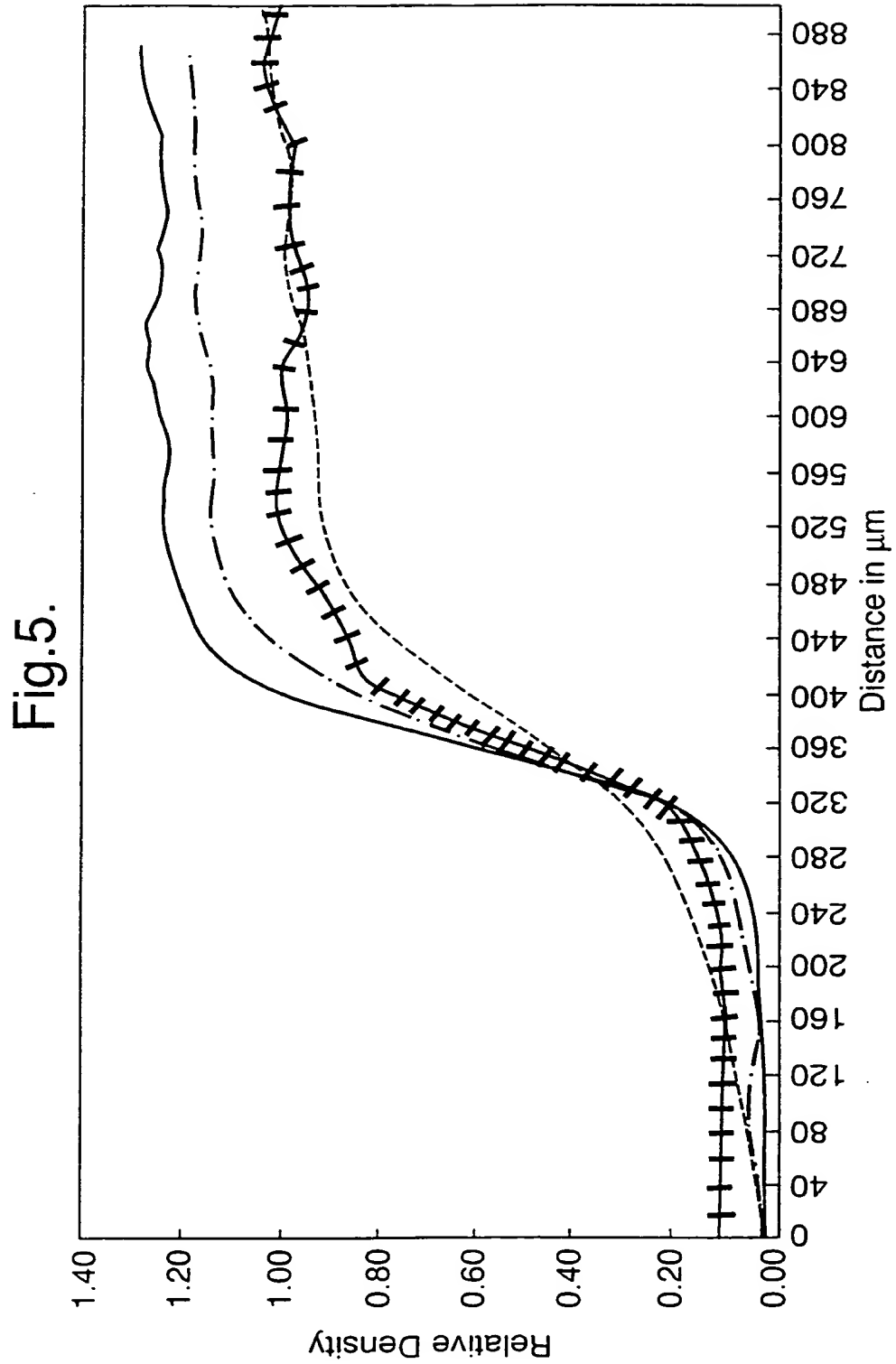


Fig.2.









PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference HCM/C280.01/I	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 00/ 02163	International filing date (day/month/year) 05/06/2000	(Earliest) Priority Date (day/month/year) 08/06/1999
Applicant IMPERIAL CHEMICAL INDUSTRIES PLC		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 02 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the title,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the abstract,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure N .



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/02163

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B41M5/00 G03G7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B41M G03G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ✓	EP 0 785 088 A (AGFA GEVAERT NV) 23 July 1997 (1997-07-23) page 2, line 48 - line 52 page 4, line 44 - line 52	1-16
Y	page 5, line 8 - line 20	17-20
Y ✓	WO 96 34766 A (ICI PLC ;BRADBURY ROY (GB); MOSCROP CLIVE (GB); SLARK ANDREW (GB);) 7 November 1996 (1996-11-07) cited in the application page 4, line 7 -page 13, line 15 page 16, line 18 - line 25	17-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

8 August 2000

Date of mailing of the international search report

17/08/2000

Name and mailing address of the ISA

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 Fax: (+31-70) 340-3016

Authorized officer

Markham, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/02163

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0785088	A	23-07-1997	JP	9193560 A	29-07-1997
WO 9634766	A	07-11-1996	DE	69603952 D	30-09-1999
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			EP	0823927 A	18-02-1998
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			JP	11504958 T	11-05-1999
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			US	6037309 A	14-03-2000

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 344 933 (MIKOSHIBA HISASHI ET AL) 6 September 1994 see column 2, line 35 - column 3, line 25 see column 11, line 3 - line 6 see dye 30. see column 41, line 27 - line 48 ---	1-17
X	DE,A,38 29 918 (FUJI PHOTO FILM CO LTD) 16 March 1989 see page 3, line 45 - page 4, line 59 see page 5, line 55 - line 56 see dyes 15,16 ---	1-17
X	EP,A,0 613 783 (DAINIPPON PRINTING CO LTD) 7 September 1994 see page 2, line 3 - line 53 see page 3, line 15 - page 4, line 9 see Table 1, Example 1-2 see Examples , Table 8 ---	1-17
X	EP,A,0 400 706 (AGFA GEVAERT NV) 5 December 1990 see page 3, line 34 - page 4, line 54 see table 1, dyes 1.51, 1.66 ---	1-17
X	EP,A,0 327 077 (DAINIPPON PRINTING CO LTD) 9 August 1989 see page 2, line 55 - page 3, line 40 see Table 1, No. 5 see Example 1, Table 2 ---	1-17
X	EP,A,0 229 374 (EASTMAN KODAK CO) 22 July 1987 see page 3, line 25 - page 4, line 14 see Compound No. 7 see Example 3, Table 5 ---	1-17
X	EP,A,0 582 324 (DAINIPPON PRINTING CO LTD) 9 February 1994 see page 2, line 51 - line 58 see page 13, line 55 - page 16, line 20 see Table D1, Nos. 2,14,20, Table D2, Nos. 2,14 see example D ---	1-17
X	EP,A,0 526 170 (MITSUI TOATSU CHEMICALS) 3 February 1993 see page 2, line 1 - page 3, line 36 see example 5 ---	1-17
1 X	EP,A,0 468 380 (SONY CORP) 29 January 1992 see page 2, line 28 - line 57 see EXAMPLE 11, DYE 11 ---	1-17
	--- -/--	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 96/01027

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-A- 60260060	23-12-85
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		JP-C- 1802862	26-11-93
		JP-B- 5013075	19-02-93
		JP-A- 60260381	23-12-85
		DE-A- 3520227	12-12-85
		FR-A- 2565528	13-12-85
		US-A- 4614521	30-09-86

US-A-3940246	24-02-76	CH-B- 560285	27-03-75
		AU-B- 4129972	25-10-73
		BE-A- 782603	25-10-72
		CH-A- 606971	30-09-74
		DE-A- 2219978	16-11-72
		FR-A- 2136457	22-12-72
		GB-A- 1395188	21-05-75
		LU-A- 65236	24-10-73
		NL-A- 7205589	30-10-72
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		US-A- 4078886	14-03-78

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		CH-A- 606971	30-09-74
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		LU-A- 65236	24-10-73
		NL-A- 7205589	30-10-72
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		US-A- 3782896	01-01-74
		US-A- 3940246	24-02-76
		US-A- 4029467	14-06-77
		US-A- 4078886	14-03-78

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 96/01027

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0582324		DE-D- 69012745	27-10-94
		DE-T- 69012745	18-05-95
		EP-A- 0427867	22-05-91
		WO-A- 9013435	15-11-90
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		JP-A- 5185752	27-07-93
		KR-B- 9510648	21-09-95
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		JP-A- 54053009	26-04-79

EP-A-0655345	31-05-95	JP-A- 7144478	06-06-95
		US-A- 5507839	16-04-96

INTERNATIONAL SEARCH REPORT

Intern Application No
PCT/US 00/02163

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B41M5/00 G03G7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B41M G03G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 785 082 A (AGFA GEVAERT NV) 23 July 1997 (1997-07-23) page 2, line 48 - line 52 page 4, line 44 - line 52	1-16
Y	page 5, line 8 - line 20	17-20
Y	WO 96 34766 A (ICI PLC ;BRADBURY ROY (GB); MOSCROP CLIVE (GB); SLARK ANDREW (GB);) 7 November 1996 (1996-11-07) cited in the application page 4, line 7 -page 13, line 15 page 16, line 18 - line 25	17-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

8 August 2000

Date of mailing of the international search report

17/08/2000

Name and mailing address of the ISA
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Fax: (+31-70) 340-3016

Authorized officer

Markham, R

INTERNATIONAL SEARCH REPORT

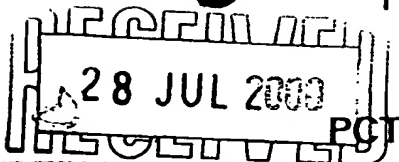
...on patent family members

International Application No

PCT/GB 00/02163

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0785088	A	23-07-1997	JP 9193560 A	29-07-1997
WO 9634766	A	07-11-1996	DE 69603952 D	30-09-1999
			DE 69603952 T	05-01-2000
			EP 0823927 A	18-02-1998
			EP 0823880 A	18-02-1998
			WO 9634916 A	07-11-1996
			JP 11504958 T	11-05-1999
			JP 11504871 T	11-05-1999
			US 6037309 A	14-03-2000

PATENT COOPERATION TREATY



From the INTERNATIONAL BUREAU

To:

KEITH W NASH & CO.
90-92 Regent Street
Cambridge CB2 1DP
ROYAUME-UNI

**NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT**

(PCT Administrative Instructions, Section 411)

Date of mailing (day/month/year) 20 July 2000 (20.07.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference HCM/C280.01/I	
International application No. PCT/GB00/02163	International filing date (day/month/year) 05 June 2000 (05.06.00)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 08 June 1999 (08.06.99)
Applicant IMPERIAL CHEMICAL INDUSTRIES PLC et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
08 June 1999 (08.06.99)	9913172.4	GB	28 June 2000 (28.06.00)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Alejandro HENNING

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference HCM/C280.01/I	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/02163	International filing date (day/month/year) 05/06/2000	Priority date (day/month/year) 08/06/1999
International Patent Classification (IPC) or national classification and IPC B41M5/00		
Applicant IMPERIAL CHEMICAL INDUSTRIES PLC et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 02/01/2001	Date of completion of this report 08.05.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Giannitsopoulos, G Telephone No. +49 89 2399 2795 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/02163

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-15 as originally filed

Claims, No.:

1-19 as received on 04/01/2001 with letter of 02/01/2001

Drawings, sheets:

1/4-4/4 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB00/02163

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary: _____

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-19
	No: Claims
Inventive step (IS)	Yes: Claims 1-19
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-19
	No: Claims

**2. Citations and explanations
see separate sheet**

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/02163

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

The closest prior art is disclosed in EP-A-785088 (D1) which is directed to a dye donor element but mentions the inclusion of dendrimers as a plasticizer in the receiving layer of image receiving elements (page 5, lines 18-20).

The claimed receiver medium differs from this prior art in that the *host polymer*, in which the highly branched functionalised polymer is dispersed, has a Tg of <50°C.

The receiver medium of claim 1, the methods of claims 14 and 15 and the combination of claim 16 are therefore novel.

The object of the present invention is to provide a receiver medium for digital imaging which does not show the problems discussed in the passage from page 3, line 6 to page 4, penultimate paragraph.

This object is achieved in accordance with the invention claimed in the independent claims, which is neither taught nor suggested by any combination of the teachings of the two available citations. Since the claimed subject matter is not rendered obvious by the prior art citations on file, it involves an inventive step.

Claims

1. A receiver medium for digital imaging, comprising a substrate having a dye-receiving surface bearing a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer, wherein the host polymer has a Tg of $<50^{\circ}\text{C}$.
2. A receiver medium according to claim 1, wherein at least some of the end groups of the highly branched polymer carrying functional groups selected from OH, NH_2 , NHR, NR_2 , COOH, CONH_2 , NHCOR , CONHR , SO_2NH_2 , SO_2NHR , SO_3H , NHCONH_2 , NHCONHR , $=\text{NOH}$ and PO_3H , in which R is selected from CH, NO_2 , Cl, F, Br, $\text{C}_{1-6}\text{alkyl}$, $\text{C}_{1-6}\text{alkoxy}$, $\text{NHCOC}_{1-6}\text{alkyl}$, NHCophenyl , $\text{NHSO}_2\text{alkyl}$, $\text{NHSO}_2\text{phenyl}$ and aryloxy, and preferably from the groups having at least one H atom.
3. A receiver medium according to claim 1 or 2, wherein at least 50%, preferably at least 70%, of the end groups of the highly branched polymer carry functional groups.
4. A receiver medium according to any one of the preceding claims, wherein the highly branched polymer has a molecular weight of at least 1000.
5. A receiver medium according to any one of the preceding claims, wherein the radius of gyration of the highly branched polymer is in the range 2 to 10nm.
6. A receiver medium according to any one of the preceding claims, wherein the host polymer is selected from polymers including polyesters, acrylic polymers, vinyl polymers, poly(vinyl pyridine), vinyl pyrrolidone/vinyl acetate, vinyl chloride/vinyl acetate copolymers, and cellulosic polymers.
7. A receiver medium according to any one of the preceding claims, when the highly branched polymer is present in an amount in the range 10 to 90%, preferably 20 to 60%, by weight of the coating.

8. A receiver medium according to any one of the preceding claims, wherein the substrate is in the form of a film or sheet of material.
9. A receiver medium according to any one of the preceding claims, wherein the substrate is pre-treated prior to application of the coating.
10. A receiver medium according to any one of the preceding claims, wherein the coating has a thickness in the range $1\mu\text{m}$ to $100\mu\text{m}$, preferably $50\mu\text{m}$ or less, especially in the range from $2\mu\text{m}$ to $10\mu\text{m}$, for media for use in thermal dye transfer printing and in the range $10\mu\text{m}$ to $50\mu\text{m}$ for media for use in ink jet printing
11. A receiver medium according to any one of the preceding claims, wherein the coating includes particulate filler material.
12. A receiver medium according to any one of the preceding claims, including a top coat over the coating.
13. A receiver medium according to any one of the preceding claims, including one or more back coats on the side of the substrate remote from the dye-receiving surface.
14. A method of making a receiver medium, comprising applying to a dye-receiving surface of a substrate a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer, wherein the host polymer has a $T_g < 50^\circ\text{C}$.
15. A method of printing, comprising applying dye to the dye-receiving surface of receiver medium in accordance with any one of claims 1 to 13 by a digital imaging technique.
16. A digital imaging receiver medium/dye combination in which the receiver medium comprises a substrate having a dye-receiving surface bearing a coating comprising a highly branched functionalised polymer of generally globular form dispersed in a host polymer having a $T_g < 50^\circ\text{C}$, and the dye is capable of interacting with the highly branched polymer.

17. A combination according to claim 16, wherein the receiver medium is in accordance with any one of claims 2 to 13.

18. A combination according to claim 16 or 17, wherein the dye has functional groups complementary to functional groups of the highly branched polymer.

19. A combination according to claim 16, 17 or 18, wherein the highly branched polymer and dye are capable of interacting by acid-base reaction.

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum)

HCM/C280.01/I

Box No. I TITLE OF INVENTION

Receiver Medium for Digital Imaging

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Imperial Chemical Industries PLC
Imperial Chemical House
Millbank
London SW1P 3JF
United Kingdom

☐ This person is also inventor.

Telephone No.

Facsimile No.

Teleprinter No.

State (that is, country) of nationality:

GB

State (that is, country) of residence:

GB

This person is applicant
for the purposes of:

☐ all designated
States

☒ all designated States except
the United States of America

☐ the United States
of America only

☐ the States indicated in
the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

BUTTERS, Alan
17 Mowlands, Capel St Mary
Suffolk, IP9 2XB
United Kingdom

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box
is marked, do not fill in below.)

State (that is, country) of nationality:

GB

State (that is, country) of residence:

GB

This person is applicant
for the purposes of:

☐ all designated
States

☐ all designated States except
the United States of America

☒ the United States
of America only

☐ the States indicated in
the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf
of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

Keith W Nash & Co
90-92 Regent Street
Cambridge
CB2 1DP
United Kingdom

Telephone No.

01223 355477

Facsimile No.

01223 324353

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

CLIFTON, Andrew
1 Norwich Road
Claydon
Ipswich, IP6 0DQ
United Kingdom

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

GB

State (that is, country) of residence:

GB

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

- ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☐ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|-------------------------------------------------------------------|-----------------------------------------------------------------------|
| <input type="checkbox"/> AE United Arab Emirates | <input type="checkbox"/> LR Liberia |
| <input type="checkbox"/> AL Albania | <input type="checkbox"/> LS Lesotho |
| <input type="checkbox"/> AM Armenia | <input type="checkbox"/> LT Lithuania |
| <input type="checkbox"/> AT Austria | <input type="checkbox"/> LU Luxembourg |
| <input type="checkbox"/> AU Australia | <input type="checkbox"/> LV Latvia |
| <input type="checkbox"/> AZ Azerbaijan | <input type="checkbox"/> MA Morocco |
| <input type="checkbox"/> BA Bosnia and Herzegovina | <input type="checkbox"/> MD Republic of Moldova |
| <input type="checkbox"/> BB Barbados | <input type="checkbox"/> MG Madagascar |
| <input type="checkbox"/> BG Bulgaria | <input type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input type="checkbox"/> BR Brazil | <input type="checkbox"/> MN Mongolia |
| <input type="checkbox"/> BY Belarus | <input type="checkbox"/> MW Malawi |
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| <input type="checkbox"/> CN China | <input type="checkbox"/> NZ New Zealand |
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| <input type="checkbox"/> CU Cuba | <input type="checkbox"/> PT Portugal |
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| <input type="checkbox"/> DK Denmark | <input type="checkbox"/> SD Sudan |
| <input type="checkbox"/> DM Dominica | <input type="checkbox"/> SE Sweden |
| <input type="checkbox"/> EE Estonia | <input type="checkbox"/> SG Singapore |
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| <input type="checkbox"/> FI Finland | <input type="checkbox"/> SK Slovakia |
| <input type="checkbox"/> GB United Kingdom | <input type="checkbox"/> SL Sierra Leone |
| <input type="checkbox"/> GD Grenada | <input type="checkbox"/> TJ Tajikistan |
| <input type="checkbox"/> GE Georgia | <input type="checkbox"/> TM Turkmenistan |
| <input type="checkbox"/> GH Ghana | <input type="checkbox"/> TR Turkey |
| <input type="checkbox"/> GM Gambia | <input type="checkbox"/> TT Trinidad and Tobago |
| <input type="checkbox"/> HR Croatia | <input type="checkbox"/> TZ United Republic of Tanzania |
| <input type="checkbox"/> HU Hungary | <input type="checkbox"/> UA Ukraine |
| <input type="checkbox"/> ID Indonesia | <input type="checkbox"/> UG Uganda |
| <input type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> US United States of America |
| <input type="checkbox"/> IN India | <input type="checkbox"/> UZ Uzbekistan |
| <input type="checkbox"/> IS Iceland | <input type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> JP Japan | <input type="checkbox"/> YU Yugoslavia |
| <input type="checkbox"/> KE Kenya | <input type="checkbox"/> ZA South Africa |
| <input type="checkbox"/> KG Kyrgyzstan | <input type="checkbox"/> ZW Zimbabwe |
| <input type="checkbox"/> KP Democratic People's Republic of Korea | |
| <input type="checkbox"/> KR Republic of Korea | |
| <input type="checkbox"/> KZ Kazakhstan | |
| <input type="checkbox"/> LC Saint Lucia | |
| <input type="checkbox"/> LK Sri Lanka | |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM☐ Further priority claims are indicated in the Supplemental Box.

Filing date of earlier application (day-month-year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 08.06.1999 8 June 1999	9913172.4	GB		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): **GB 9913172.4**

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(h)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA)
(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day-month-year)

Number

Country (or regional Office)

ISA /

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 4
description (excluding sequence listing part) : 15
claims : 3
abstract : 1
drawings : 3
sequence listing part of description : _____

Total number of sheets : 26

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☒ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☒ priority document(s) identified in Box No. VI as item(s): **GB 9913172.4**
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☐ other (specify):

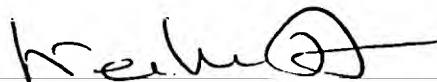
Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

English

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).



Keith W Nash & Co, Agents

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1. Date of actual receipt of the purported international application:	2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	
6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.	

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Date of receipt of the record copy by the International Bureau:

This sheet is not part of and does not count as a sheet of the international application.

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FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International application No.

Date stamp of the receiving Office

Applicant's or agent's
file reference

HCM/C280.01/I

Applicant

Imperial Chemical Industries PLC

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 55.00 T

2. SEARCH FEE 605.00 S

International search to be carried out by

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

The international application contains 26 sheets.

first 30 sheets 264.00 b1

remaining sheets additional amount = b2

Add amounts entered at b1 and b2 and enter total at B 264.00 B

Designation Fees

The international application contains 3 designations.

3 x £56 = 168.00 D

number of designation fees
payable (maximum 8) amount of designation fee

Add amounts entered at B and D and enter total at I 432.00 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) 22.00 P

5. TOTAL FEES PAYABLE 1114.00

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☐ authorization to charge
deposit account (see below)

☐ bank draft

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☒ cheque

☐ cash

☐ other (specify):

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☐ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

Deposit Account No.

Date (day/month/year)

Signature